

Such polymerizable adhesives may also comprise inorganic fillers, organic fillers, pigments, colors, dyes, surface active agents, opacifiers, radioopaque agents, and other modificants. Accordingly, it may be preferred in the practice of certain embodiments of this invention to admix the polymerizable adhesives of this invention with various amounts of fillers or other modificants. Thus, the adhesives may be admixed with fillers such as, for example, silica, quartz, etc. in weight ratios of up to about 1:6. It is frequently desirable to add fillers to the adhesives of this invention in amounts sufficient to render the compositions thixotropic so as to promote ease of handling and good physical properties. Accordingly, filled compositions may be formulated having up to about 80% by weight of filler or other modificant. Such filled or otherwise modified compositions are within the scope of this invention.

In general, the adhesives of this invention may be formulated by mixing together the selected components. Accordingly, it is generally necessary only to mix the silaneous species together with the non-silaneous polymerizable compounds (if any) and to add thereto the selected photosensitizing systems, along with the optional fillers, pigments, and other modificants. Thereafter, it is usually helpful to degas the formulation and/or to allow the formulation to stand for from about 6 hours to about 7 days to allow full homogenization and dispersion of the components of the mixture. Although these adhesives are light curable, preparation and storage away from incidental light is usually not necessary due to their remarkable stability to low ambient light levels. In use, the materials of this invention are simply dispensed as desired and exposed to light of the appropriate wavelength at a convenient, effective, intensity. Accordingly, either visible, ultraviolet or broad spectrum light, depending upon the photosensitizing system selected, is directed to the dispensed adhesive for a time sufficient to allow the adhesive to cure. This may be done using any convenient light source. Thus, a visible light curing unit, such as the Prisma-Lite™, unit of the L. D. Caulk Co., may be used to expose visible light curable adhesives. The Caulk Nuva-Lite® source may be used for ultraviolet polymerization of the adhesives of this invention having ultraviolet photosensitizing systems. In general, it is necessary only to expose the adhesives of this invention to relatively low levels of irradiation in order to secure polymerization. Thus, typical formulations may be exposed to a 0.4 watt/cm²/sec visible light for approximately 30 seconds to effect cures of up to about 6 millimeters in depth.

The adhesives of this invention are well adapted to industrial fixturing processes, and for other adhesive uses including uses in dentistry. Accordingly, such adhesives may be applied to a selection of articles to be "fixed" with respect to each other, the articles are then positioned as desired and the adhesive demand set to effect a rapid stabilization of the configuration of such articles. Such fixturing may be followed, optionally, by further configuration stabilization such as by application of additional adhesives, filling materials, or other compositions.

The adhesives of this invention are particularly suited for use in dentistry. Accordingly, they may be used in the construction and application of crowns and bridges, dental veneers, orthodontic appliances, and numerous other oral applications. The high water resistivity of such adhesives make them particularly suited for such uses. To practice the inventive process for filling teeth

it is necessary only to apply the silaneous adhesives of the present invention, preferably those having substantial loadings of particulate, inorganic filler and exposing the adhesive to actinic light in a biologically compatible fashion. Most preferably, the ratio of resin to filler loadings of such materials are from about 1:2 to about 1:5.

The following examples are included by way of illustration only and are not to be construed as limiting.

EXAMPLE 1

A polymerizable resin was formulated by blending together the following constituents:

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| Epocryl™ 370 (a glycidyl acrylate of bisphenol-A, Shell Co.) | 2.0 g |
| 3-methacryloxypropyltrimethoxysilane | 7.4 g |
| Vinyl-tris(methoxyethoxy)silane | 1.19 g |
| Benzoyl peroxide | 1.01 g |
| Camphoroquinone | 1.1 g |
| Methyl diethanolamine | 1.3 g |
| | 0.0 g |

The blend was allowed to stand in the dark for approximately 12 hours at which time a hazy-clear, fluid, uniform blend was evidenced. The blend was degassed under vacuum several times and filled into a mold having a depth of 6.5 mm. The filled mold was exposed to light from a Caulk Prisma-Lite™ unit producing a spectrum of light of 400-500 nm with a power of 0.4 w/cm²/sec for 30 seconds. A complete, rubbery cure resulted which was uniform throughout the depth of the mold.

EXAMPLE 2

A treated, inorganic filler was prepared by mixing together 97.5 g of particulated quartz of size less than 100 mesh with 2.0 g of 3-methacryloxypropyltrimethoxysilane and 0.5 g of Dow-Corning silicone surfactant 193. This treated filler was allowed to stand until the quartz was no longer "dusty" at which time it was milled in a ball mill for approximately 1 hour.

6.5 g of the above-described filler was blended with a mixture of 2.0 g of the formulation of Example 1 and an optional quantity of a suspending agent such as 0.04 g of Aerosil™ R-972. An additional 2.0 g of the treated quartz filler could be added resulting a total of 8.5 g of filler in 10.54 g of total weight. This filled composition was repeatedly degassed under vacuum and stored in the dark. Exposure to light from Prisma-Lite™ unit for approximately 10 seconds yielding curing to a depth of approximately 5 mm. Exposure for an additional 10 seconds yielded total curing depths of approximately 6 mm. This filled adhesive is especially suitable for use as a high temperature demand set adhesive.

EXAMPLE 3

A filled, restorative adhesive suitable for dental, industrial, and other uses was formulated as follows:

A silane resin was constituted from 20 g of Nupol™ 46-4005 (Freeman), which is a bis-GMA 79 g of 3-methacryloxypropyltrimethoxysilane, and 1 g of Dow-Corning silicone surfactant 193. 24.4 g of pyrogenic silica (Aerosil™ OX-50) was blended with 0.6 g of the foregoing silane resin to form a treated filler. An acrylic resin was formulated from 19.64 g of the hexamethylene diisocyanate adduct of bis-GMA, 0.04 g of camphoroquinone, 0.2 g of methyl diethanolamine, and 0.12